91602
new 82-10

LEGAL NOTICE

This report was prepared by Ontario Hydro and, while effort has been made to assure the accuracy and applicability of the material contained herein, neither Ontario Hydro nor any person acting on its behalf:

(a) makes any warranty, express or implied with respect to the use of any information, apparatus, method or process disclosed in this report or that such use may not infringe privately owned rights; or

(b) assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

ontario hydro
research division

ENHANCED HYDROGEN DIFFUSION AND REMOVAL TECHNIQUES BY ELECTROMIGRATION

Report No. 90-51-K

K. Tashiro
Engineer
Materials Integrity Section
Metallurgical Research Department

ABSTRACT

This report summarizes the effects seen when hydrogen in zirconium is subjected to an electric field. Under the influence of an electric field, hydrogen moves towards the negative end of the sample. If the hydrogen is not allowed to escape, hydrogen concentration at the negative end will build up until the resulting electric field effect is negated by the concentration gradient formed by the electric field. However, if a path for the escape of hydrogen is provided, the hydrogen can be removed and forced into metals which under normal conditions will not accept hydrogen from zirconium. Therefore, it is a normal extension that a metal which accepts hydrogen from zirconium normally, such as yttrium can enhance its overall sink properties by driving the hydrogen into the sink by an electric field rather than allowing a concentration gradient driving force only.

job	file	date	report no.
84-101-451	823.21	April 6, 1990	90-51-K

90-06098/

ontario hydro
research division

EXECUTIVE SUMMARY

ENHANCED HYDROGEN DIFFUSION AND REMOVAL TECHNIQUES BY ELECTROMIGRATION

K. Tashiro
Materials Integrity Section
Metallurgical Research Department

The absorption of deuterium into zirconium is recognized as the current life limiting factor of Zr-2.5 Nb pressure tubes. Large deuterium pickup rates are mainly found at the inlet and especially at the outlet ends whereas the remaining portion of the tube does not exhibit a large hydrogen concentration and therefore possesses a large amount of remaining life. It could be advantageous to redistribute this deuterium peak or remove it locally.

This report describes the preliminary results of the effects of an electric field on hydrogen. Generally, hydrogen can be forced towards the negative end of a sample that is subjected to an electric current. This effect is a totally separate process from normal diffusion driven by concentration gradients. Therefore, this process can be seen to take a sample with a uniform hydrogen concentration and force the hydrogen to produce a concentration gradient opposite to the electric field force. This type of effect is seen only when the hydrogen is confined to the sample.

However, if a sink is provided for the hydrogen to escape, both the electric field and concentration driving forces add together to produce a greater hydrogen flux than concentration gradients alone. The sink material does not necessarily possess a greater affinity for hydrogen than zirconium but only a greater hydrogen diffusion coefficient. Therefore, materials which would normally release hydrogen to zirconium can be made to accept hydrogen from zirconium.

Future work should be carried out to investigate this process further. Quantification of this effect and a study of its practical applications should be carried out.

job	file	date	report no
84-101-451	823.21	April 6, 1990	90-51-K

TABLE OF CONTENTS

		PAGE
1.0	INTRODUCTION	1
2.0	EXPERIMENTAL METHOD	1
3.0	EXPERIMENTAL RESULTS	2
4.0	DISCUSSION	2
5.0	SUMMARY	3
6.0	FURTHER WORK	4
7.0	ACKNOWLEDGEMENTS	4
REFERENCES		5
DISTRIBUTION		LAST PAGE

TO: Dr. D. Mills
Director of Research

ontario hydro
research division

ENHANCED HYDROGEN DIFFUSION AND
REMOVAL TECHNIQUES BY ELECTROMIGRATION

1.0 INTRODUCTION

One of the major parameters to determine fitness for service of Zr-2.5 Nb pressure tubes in CANDU reactors is the absence of hydrides (deuterides) near operating temperatures. Unfortunately, due to some process, the effective deuterium pickup rates are found to be large at the inlet and outlet ends. This results in large deuterium concentration peaks at the ends of the pressure tube. The remaining body of the tube does not exhibit such a large deuterium concentration and therefore possesses a greater amount of remaining life. It would be advantageous to pressure tube life to be able to redistribute the deuterium peaks or remove them locally.

In order for a hydrogen isotope to migrate, it must be driven by some force. This force can be derived from a concentration gradient or a temperature gradient. Another force can be generated from an electric field. This force is highly controllable since its magnitude and direction are determined by the total current flow and direction.

The behaviour of hydrogen in Zr-2.5Nb under the influence of an electric field is presented in this report. The magnitude of the effect and its potential applications as a removal technique are described.

2.0 EXPERIMENTAL METHOD

Four samples with dimensions 23x2x1 mm were heavily surface hydrided to give an effective total concentration well above 200 ppm. The samples were diffusion annealed at 300°C for 24 hours. The hydride layer was not removed in order to provided an additional source of hydrogen. These samples were then configured as shown schematically in Figure 1. A 0.5 mm diameter palladium wire was welded to two samples in order to form a metallurgical bond. The other samples had a copper wire clamped onto the sample surface. A current of 20 amperes was passed through all samples. Two samples were held at 250°C with the other two at room temperature for a period of 12 days. The samples in the furnace were then air cooled.

3.0 EXPERIMENTAL RESULTS

Three distinct microstructures were observed at the conclusion of the experiment:

The first microstructure as shown in Figure 2 was exhibited by both of the room temperature samples. Essentially, there was no change in the initial hydride distribution after this treatment. This result indicates that the kinetics of diffusion and electromigration are too sluggish at room temperature.

The second and more distinct microstructure is shown in Figure 3. This microstructure is a result of electromigration without a hydrogen escape path provided. Electromigration has forced hydrogen to the negative end of the sample. Since escape of the hydrogen was not possible, the hydrogen concentration at the negative end of the sample increased. A stable concentration gradient is produced. This gradient is evident when the hydride structure is examined. Higher hydrogen concentration at the negative end produces a fine hydride structure between the large hydrides. In addition, the large hydrides are found to be longer than at the positive end. The hydride layer at the surface does not appear affected by the electromigration process.

The third microstructure is shown in Figure 4. This structure is produced when a hydrogen escape path is provided. Both electromigration and the resulting concentration gradient forces are available for hydrogen to leave at the negative terminal. This is evident by the lack of large hydrides and the dissolution of the surface hydride layer at the negative end.

4.0 DISCUSSION

The flux of hydrogen in these experiments consists of two components. The first term can be described by Fick's first law and is driven by concentration gradients alone. The second term is the flux due to an electric field. The uniaxial equation for the total flux is given as:

$$J(x) = -D\,dC/dx + CMeZE(x) \qquad (1)$$

where J(x) is the X axis hydrogen flux, M is the electric mobility of hydrogen, e is the charge of an electron, Z is the effective charge on the hydrogen atom, E(x) is the electric field strength, D is the diffusivity of hydrogen and C is the solid solution concentration.

In Figure 3, a hydrogen escape path was not present. This may be due to low solid solubility and diffusion of hydrogen in copper or a poor contact between the two metals. Hydrogen will continue to flow until the concentration gradient formed by electromigration opposes the electromigration force. With the hydrogen flux being zero, the solution to equation (1) is given as:

$$C(x) = Co\ \exp(MeZEx/D) \qquad (2)$$

where C(x) is the concentration profile and Co is the initial concentration. This effect is schematically shown in Figure 5.

Normally, hydrogen is absorbed by zirconium from palladium by a gettering action. However, in this situation the reverse is true. The proposed mechanism for the sinking ability of palladium under these conditions is as follows. Hydrogen can diffuse very rapidly in palladium. As hydrogen enters the palladium from the zirconium, it is quickly swept away from the

interface by the electromigration forces. This causes the palladium interface concentration to decrease. As a result of this concentration drop, the chemical potential of hydrogen is lower in the palladium than in the zirconium. This chemical potential difference as well as the electric field forces at the interface allows hydrogen to easily enter the palladium.

Since, electromigration occurs in both metals, simultaneous solution of equation (1) is required for both metals. An equilibrium will be set up at the interface of the two metals and can be easily described by a concentration ratio. Figure 6 illustrates solutions of equation (1) for both metals using the concentration ratio Keq as a boundary condition at the interface. The concentration ratio can be estimated by Sievert's law coefficients. The Sievert's coefficients at 250°C for zirconium is 1240 at%/$\sqrt{mm}$/1/ and for palladium 0.11 at%/$\sqrt{mm}$/8/. These coefficients result in an interface concentration ratio Keq of 11270. The large value of the equilibrium concentration ratio illustrates the tremendous gettering power of zirconium for hydrogen. For example, at 250°C, the solid solution solubility of hydrogen in Zr is approximately 0.3 at% H. Using the appropriate Sievert's constant, this hydrogen concentration is in equilibrium with a hydrogen partial pressure of $6x10^{-8}$ torr. If this pressure is also equilibrated with palladium, the resulting solid solution hydrogen concentration in the palladium is well below 0.0002 at% H. If the palladium wire had an initial hydrogen concentration of zero (very unlikely) then a very small amount of hydrogen would be absorbed by the palladium from the zirconium until equilibrium is reached. Since, 0.0002 at% H is required at the interface, electromigration forces upon hydrogen in palladium must be extremely strong to force the hydrogen concentration to these levels.

There are many factors which will affect the behaviour of electromigration of hydrogen. One main factor is temperature. At higher temperatures, the matrix resistivity increases, therefore, the electric field strength increases for a given current density. In addition, the diffusivity of hydrogen increases. Both of these effects should result in an increase in the total mass flow of hydrogen out of the zirconium when an escape path is provided. Unfortunately, the literature/2,3,4,5/ indicates that there is a decrease in the mobility term with increasing temperature. The mobility term is used to calculate mass flow when only an electric field is present. However, the reported decrease in the mobility term come from studies on tritium and may not be valid for hydrogen or deuterium. There may be a strong isotope effect which has been observed with other materials/6,7/.

5.0 SUMMARY

This report has described the preliminary results of the effects of an electric field on hydrogen. When a current is passed through a sample, hydrogen can be forced towards the negative end. Since electromigration is separate from the normal diffusion which is driven by concentration gradients, it can be used to enhance or oppose normal diffusion processes. Therefore, a sample initially with a uniform hydrogen concentration can be forced to exhibit a concentration gradient opposite to the electric field force when electromigration takes place. In this instance, the concentration driving force and the electric field forces cancel each other to produce a stable hydrogen concentration profile seen in Figure 2. This type of effect is only possible when the hydrogen is confined to the sample.

However, if a path is provided for the hydrogen to escape from the sample, both the electric field and concentration driving forces add together to produce a greater hydrogen flux than the concentration gradient can produce alone. In this instance, the sink material palladium does not

possess a greater affinity for hydrogen than zirconium but only a greater hydrogen diffusion constant. Therefore, materials which would normally release hydrogen to zirconium can be made to accept hydrogen from zirconium.

6.0 FURTHER WORK

Future work should be carried out to investigate this process further especially if any isotopic effects exist. Experiments should be carried out which will quantify this effect, specifically, the effective charge and mobility of the atom in the matrix must be determined. These parameters will allow calculations to determine the practicality of redistribution or removal of hydrogen isotopes in the matrix. The effects of non metallurgical interfaces to the matrix and its effects on hydrogen transport across them should also be researched.

Since, yttrium can sink hydrogen from zirconium even under normal conditions, studies into enhancing this sink property by electromigration would be useful. If hydrogen transport can be achieved across a non-metallurgical interface and electromigration is effective in enhancing transport, hydrogen removal may become a practical technique.

7.0 ACKNOWLEDGMENTS

The author wishes to thank J. Perek, H. Seahra and D. Oad for sample preparation, metallography and montage preparation.

Recommended by:

R.G. Fleck
Supervising Engineer
Materials Integrity Section

Prepared by:

K. Tashiro
Engineer
Materials Integrity Section

Approved by:

J. Brown
Manager
Metallurgical Research Department

REFERENCES

1. Douglass, D.L., The Metallurgy of Zirconium, International Atomic Energy Agency, 1971.

2. Pietrzak, R. and Rozenfeld, B., Acta Physica Polonica, A60, 757, 1981.

3. Pietrzak, R. and Rozenfeld, B., Acta Physica Polonica, A51, 511, 1977.

4. Pietrzak, R. and Rozenfeld, B., Acta Physica Polonica, A56, 31, 1979.

5. Pietrzak, R. and Rozenfeld, B., Acta Physica Polonica, A49, 341, 1976.

6. Peterson, D.T. and Jensen, C.L., Metal. Trans., 9A, 1673, 1978.

7. Mishra, B. and Sivertsen, J.M., Metal. Trans., 14A, 2255, 1983.

8. Lewis, F. A., The Palladium-Hydrogen System, Academic Press, London, 1967.

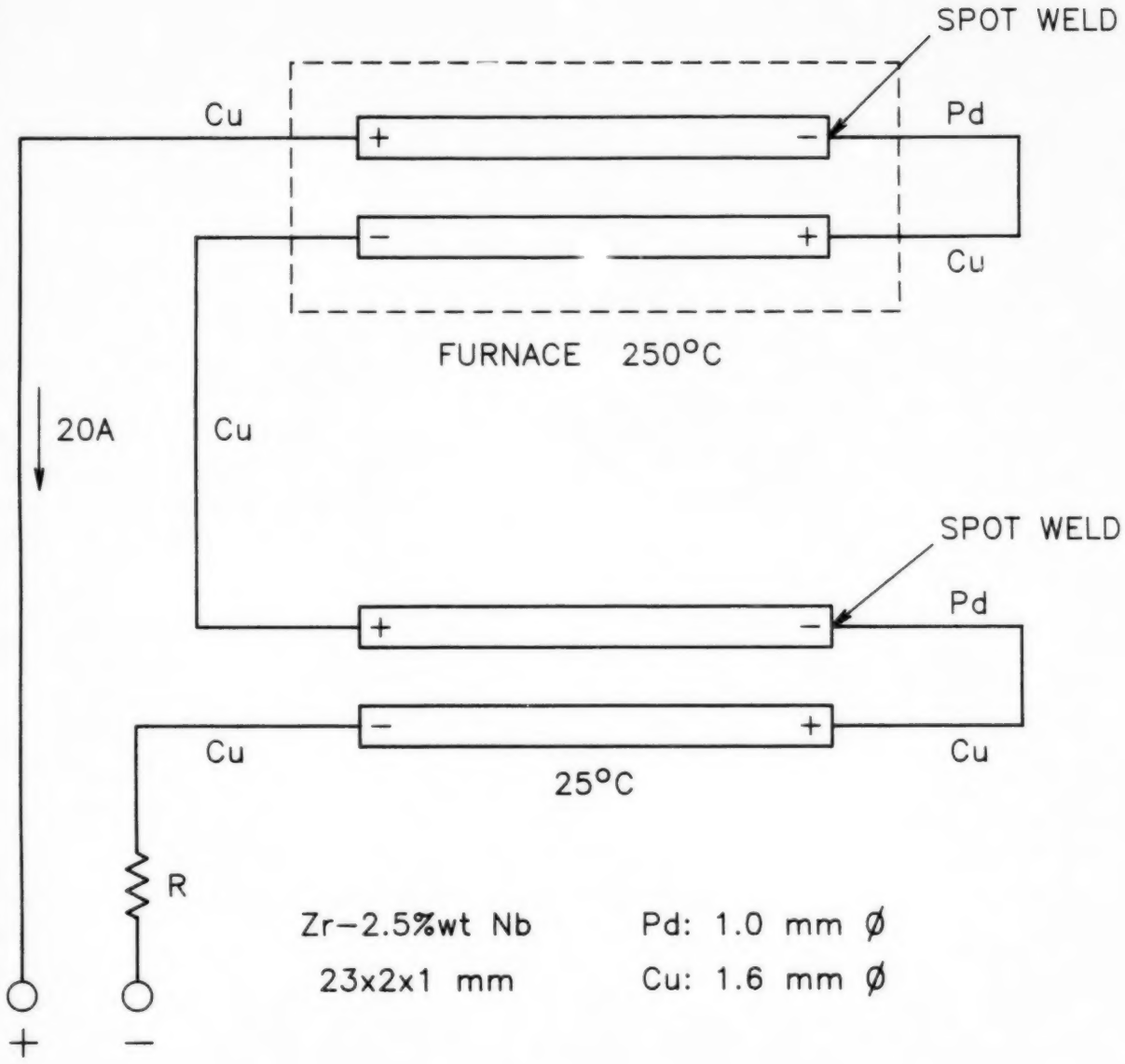

FIGURE 1 Schematic diagram of experimental setup for electromigration studies.

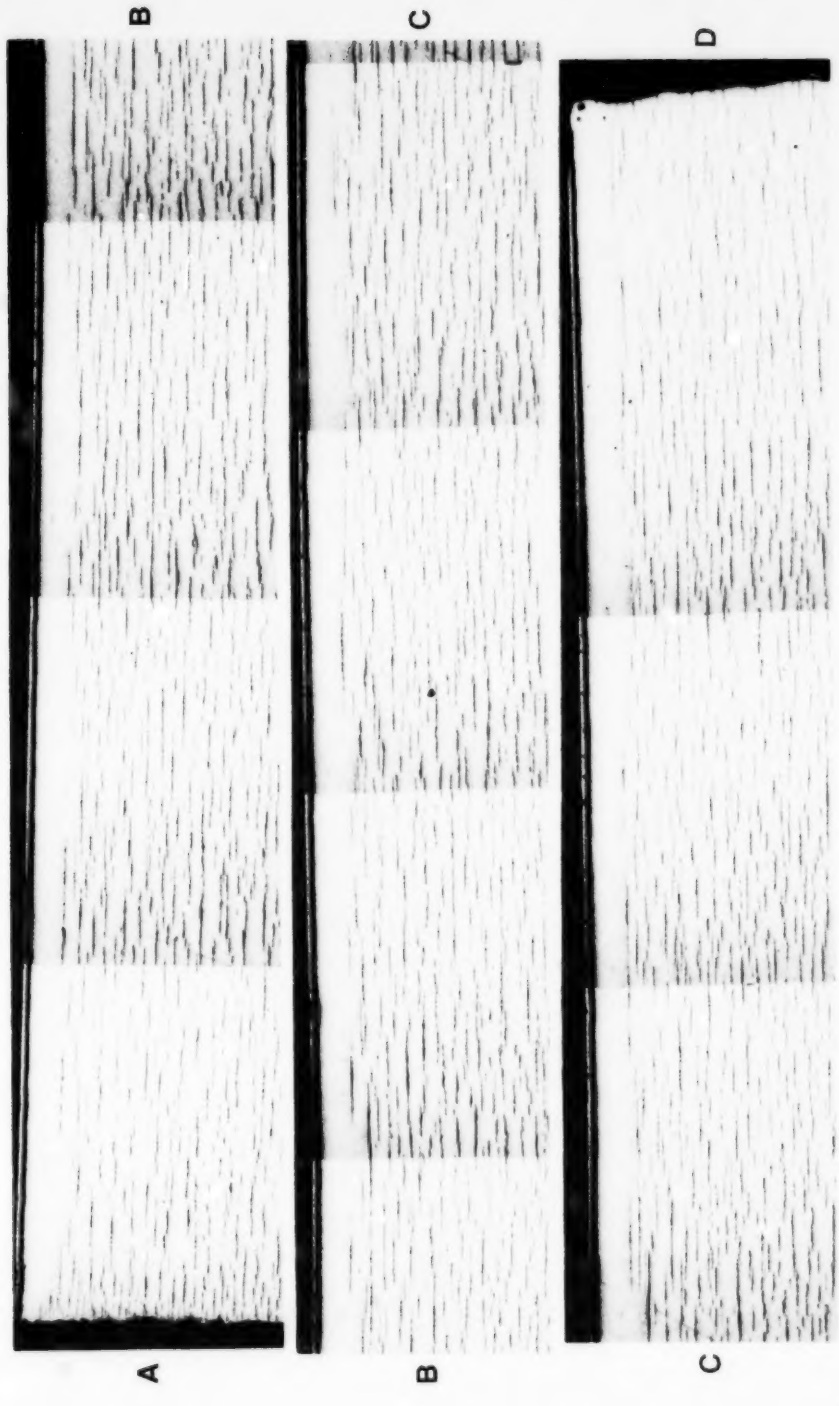

FIGURE 2 Micrograph composite illustrating electromigration effects in a Zr-2.5 Nb sample at 25°C. Generally, no electromigration effects can be seen.

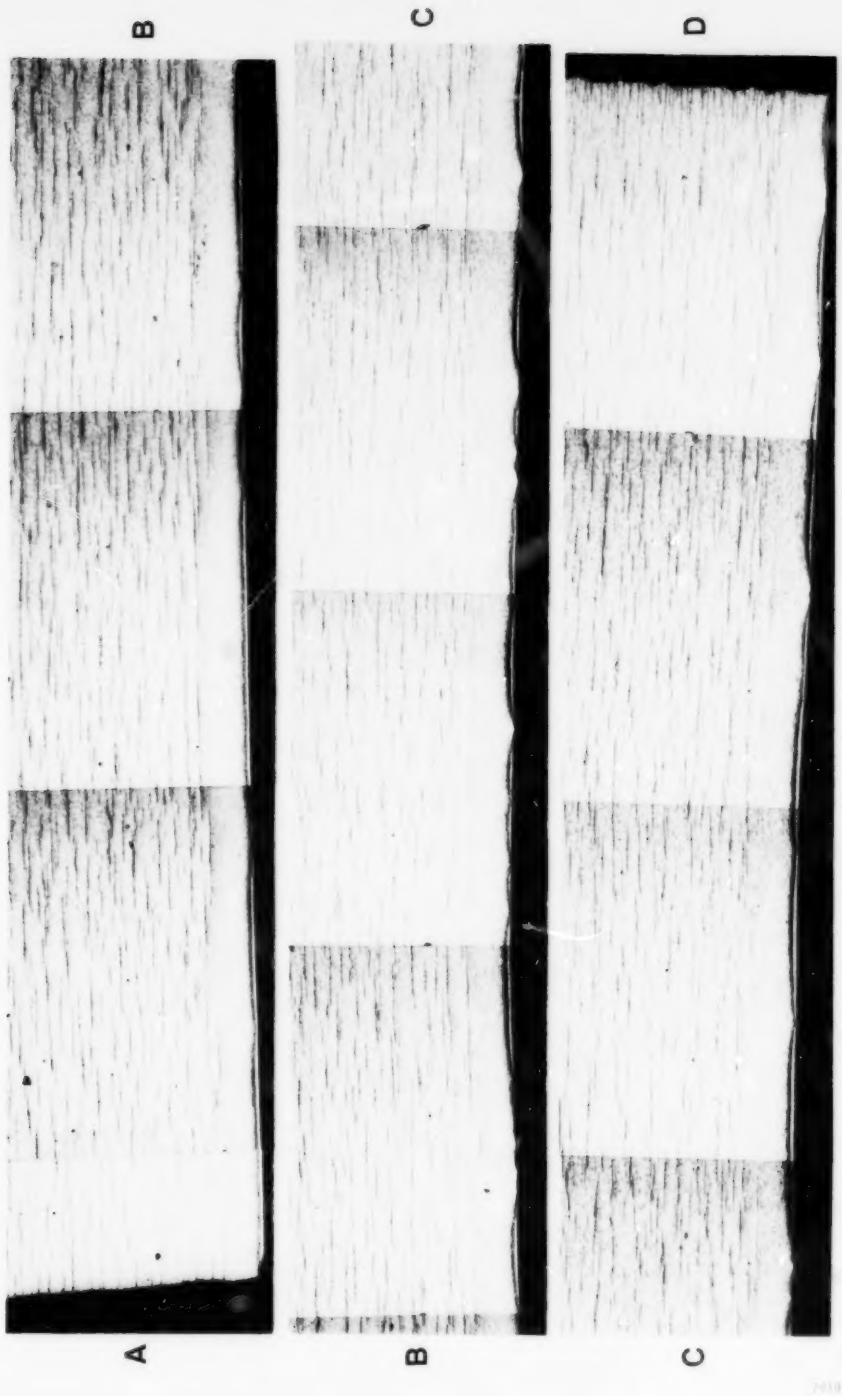

FIGURE 3 Micrograph composite illustrating electromigration effects in a Zr-2.5 Nb sample at 250°C without an escape path available. A careful comparison of the two outer ends demonstrates the higher hydrogen concentration at the negative end. This higher concentration manifests itself by a greater density of fine hydrides and longer large hydrides.

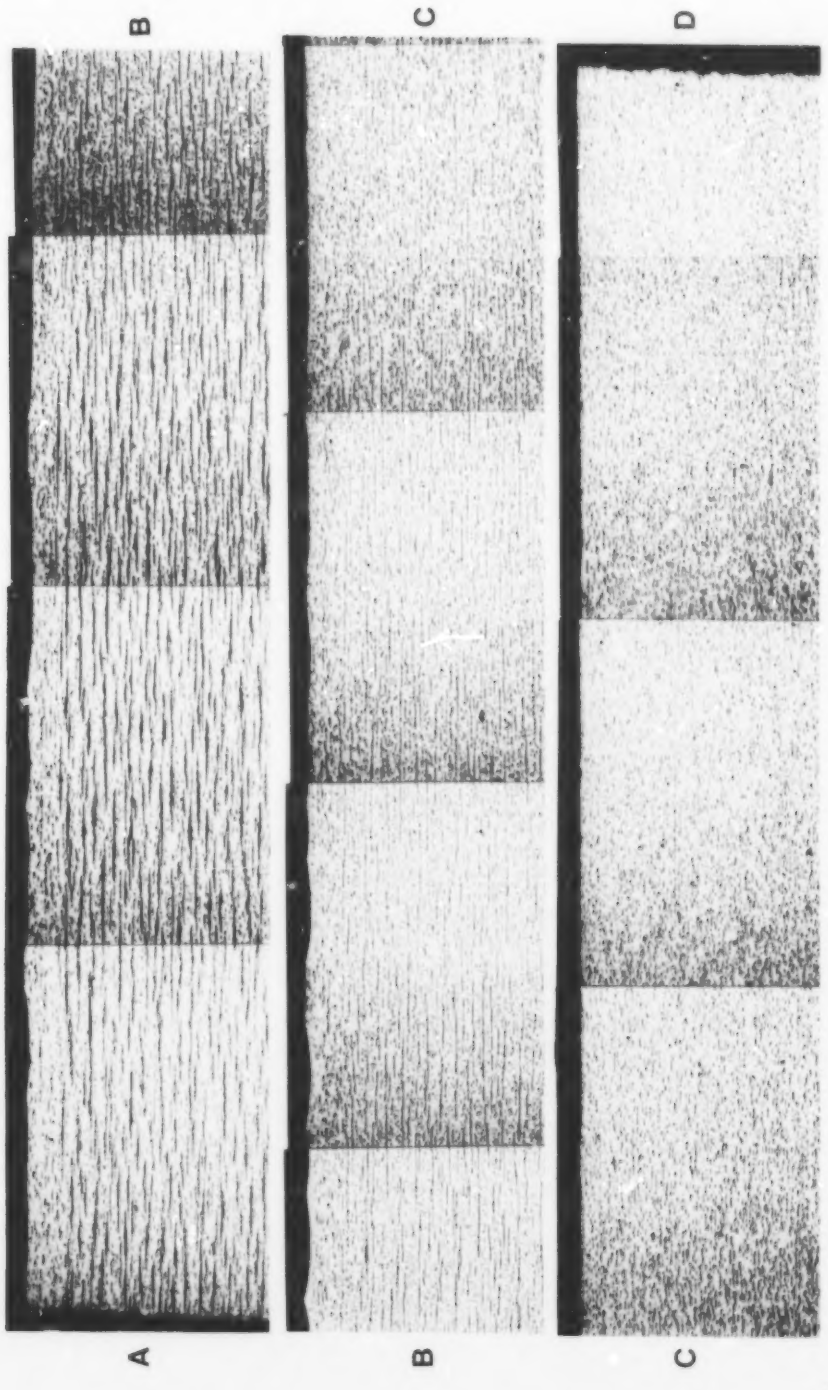

FIGURE 4 Micrograph composite illustrating electromigration effects in a Zr-2.5 Nb sample at 250°C with an escape path of palladium available. Only fine hydride is present at the negative end, indicating that TSSd (approx. 30ppm) had been reached at this temperature. The hydride layer present in the previous micrograph has been dissolved nearest the negative end.

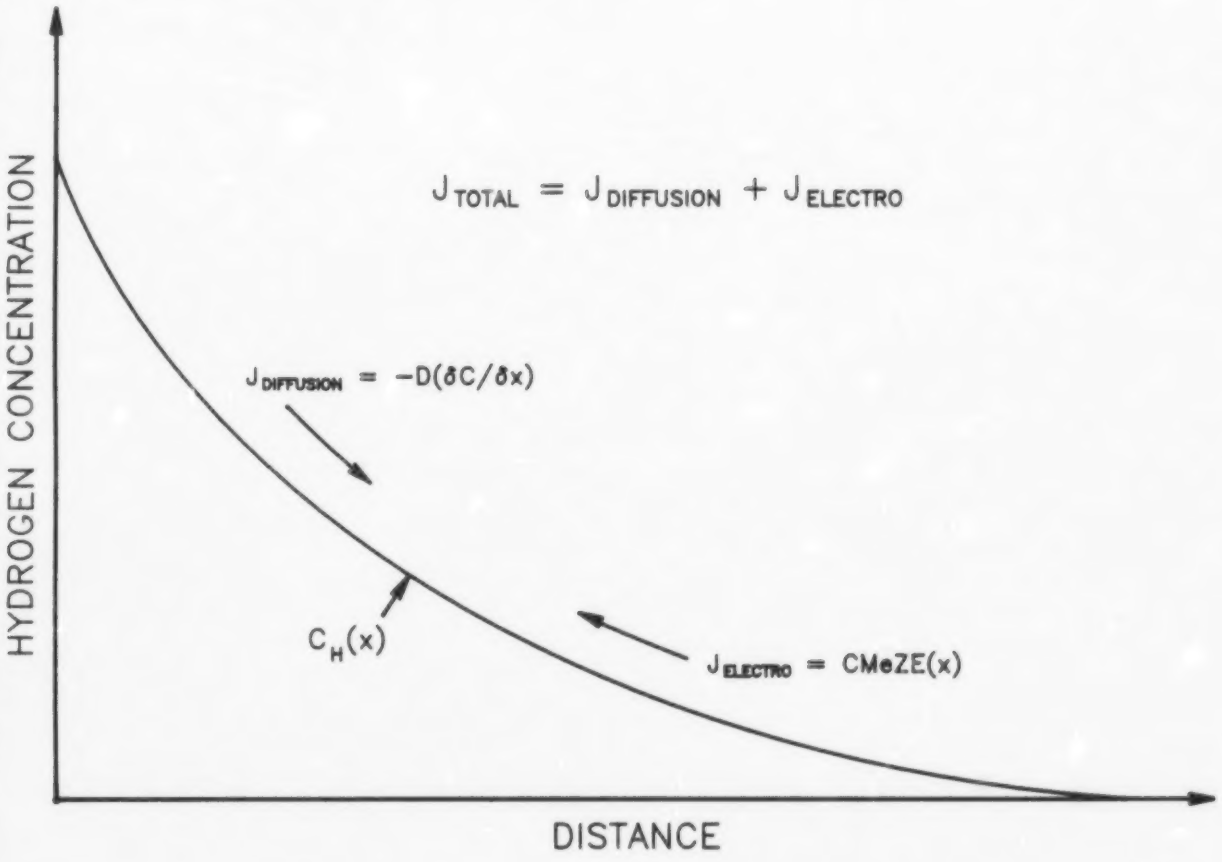

FIGURE 5 Concentration profiles in zirconium as a result of electromigration without a hydrogen escape path provided. Hydrogen is forced to the negative end by the electric field resulting in "uphill" diffusion. This will continue until the diffusional forces originating from the concentration gradients cancel out the electromigration forces.

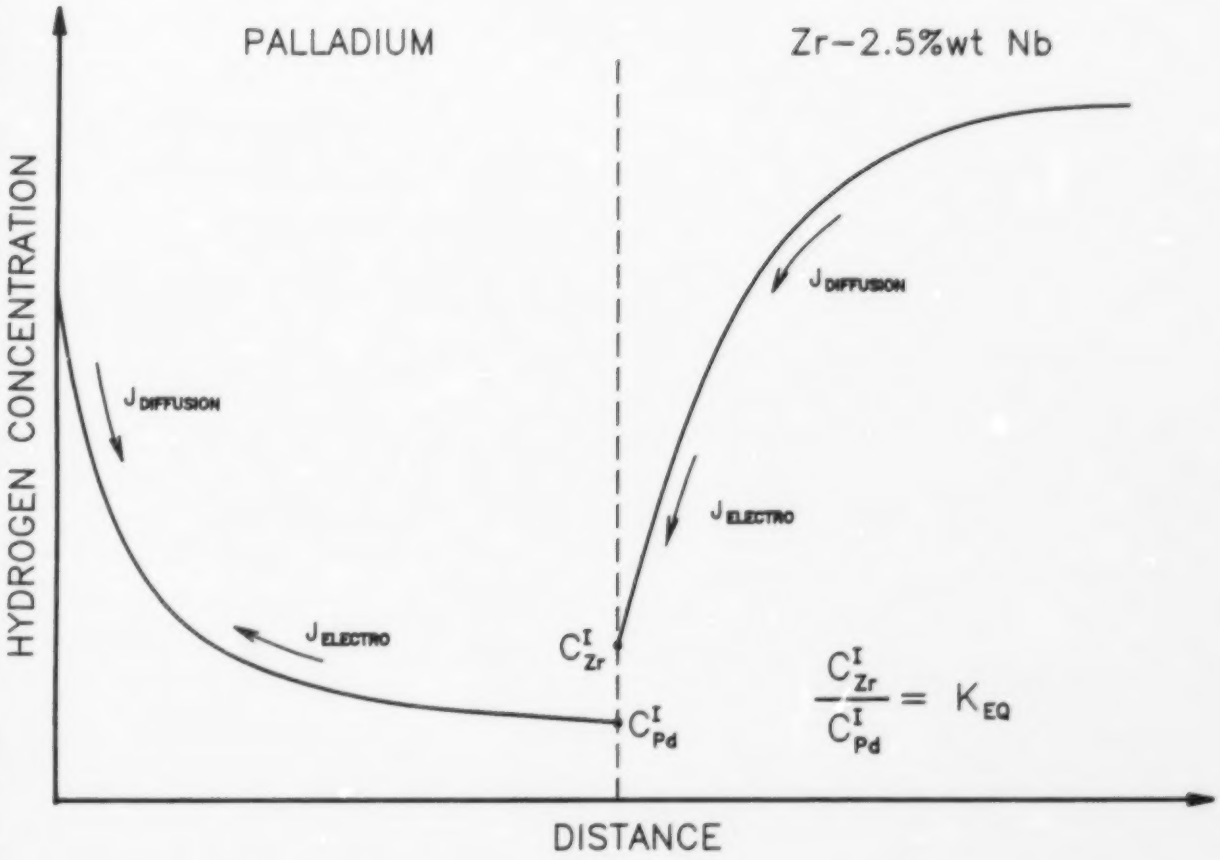

FIGURE 6 Concentration profiles in zirconium as a result of electromigration with a hydrogen escape path provided. Hydrogen is force to the negative end and leaves the zirconium matrix. The hydrogen is immediately swept from the interface area in the palladium to the negative terminal of the palladium. This process allows more hydrogen to enter the palladium. Therefore, diffusional and electromigration forces are additive in the zirconium and are subtractive in the palladium. An equilibrium is set up at the interface determined by the equilibrium constant Keq.